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(54) **Use of an additive as detergent, dispersant and anti-rust for fuels and lubricating oils**
Verwendung von Detergent, Dispersant und Antikorrosionszusätzen für Kraftstoffe und Schmieröle
Utilisation des additifs détergents, utilisation des dispersants et anticorrosifs pour combustibles et huiles lubrifiantes

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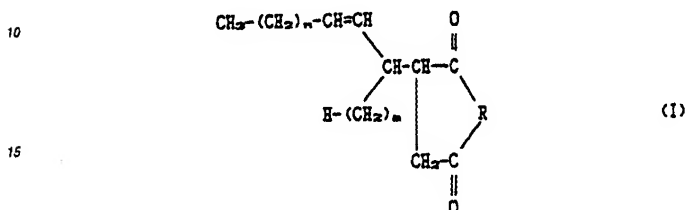
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GB-A- 1 373 411 US-A- 2 490 744
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Description

This invention relates to a use of an additive for automotive fuels and lubricating oils which possesses improved detergent, dispersant and anti-rust properties.

Said additive consists essentially of the product of condensing a mixture of alkenylsuccinic acids or anhydrides of formula (I)

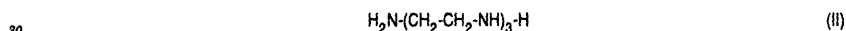


20 where:

m and n, mutually independently, represent 0 or a whole number between 1 and 10 and are such that their sum is 9 or 10, and

25 $\text{R is O or } (-\text{OH}, -\text{OH}),$

with triethylenetetramine of formula (II)



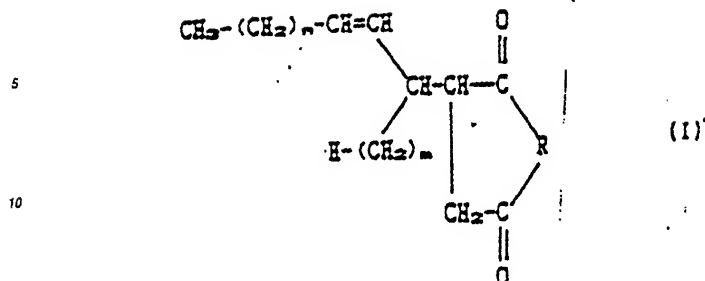
The patent literature describes several classes of alkenylsuccinimide compounds and the use of these compounds as dispersant and detergent additives in fuels and lubricants is known. By way of example, the following patent specifications can be cited:

35 US-A-3 131 150; US-A-3 172 892; US-A-3 216 936; US-A-3 287 271; US-A-3 401 118; US-A-3 717 446; US-A-3 799 877; US-A-4 048 080. US-A-4 338 205; US-A-4 548 724; and

DE-A-204 696; EP-A-0 020 037; EP-A-0 008 953; EP-A-0 299 119.

Particular mention is made of DE-A-204 696 and EP-A-0 299 119, which disclose products of reaction of alkenylsuccinic acids or anhydrides with amines as additives which provide deterging, dispersing and rust-preventing properties to fuels and lubricating oils. An objective of those skilled in art is now to improve the performances of the formulations of automotive liquid fuels or lubricants supplemented by additives of the kind referred to above by providing an improved additive which is active under particularly severe stresses, are stabler and are less expensive to produce.

The invention, therefore, provides a use of the condensation product of a blend of alkenylsuccinic acids or acid anhydrides thereof, having the formula (I):

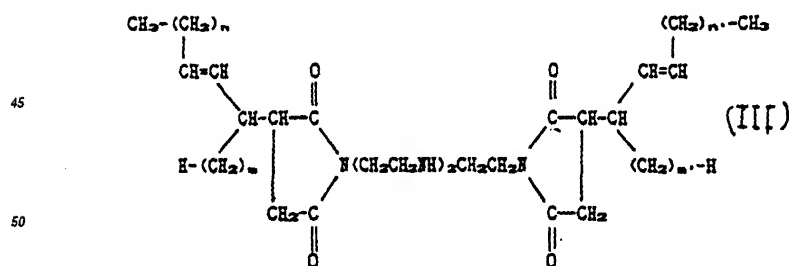


and that the condensation reaction takes place by directly heating, at a temperature of from 150°C to 200°C, a blend of (I) and (II), the molar ratio of (I) to (II) being 2,0 as an additive for improving, in an automotive liquid fuel or lubricating oil, the detergent, dispersing and rust-preventing properties.

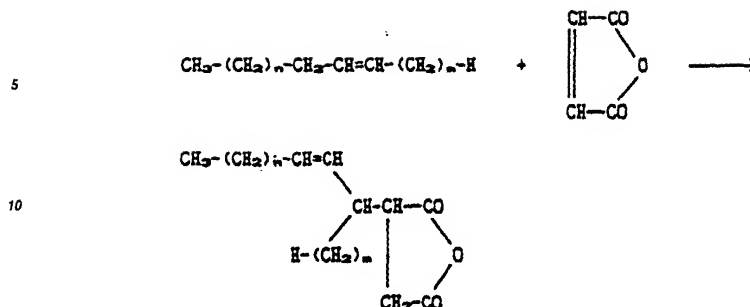
An additive prepared by the process defined above possesses excellent detergent and dispersing properties together with a remarkable rust-preventing activity, whereby the additive so prepared ensures a thorough dispersion of suspended solid particles and prevents the formation of deposits in the carburetors (or injectors as the case may be) when added to liquid fuels, while concurrently preventing the formation of rust on metal parts contacting the liquid fuels or lubricants so supplemented.

More particularly, excellent results are obtained when the alkenyl groups of (I) derive from a mixture of straight-line C_{13} and/or C_{14} monoolefins having statistically distributed double bonds along the entire aliphatic chain: a mixture of this kind can be obtained by the catalytic dehydrogenation of the corresponding normal paraffins, carried out under properly selected conditions, so as to obtain monoolefin mixtures in which the double bond is distributed statistically along the entire chain, though preferentially inside the chain.

If the condition of a molar ratio of (I) to (II) close to 2:1 is respected, the predominant product is a mixture of bis-succinimides having the general formula (III):



in which \underline{m} and \underline{n} have the meaning given heretofore, and \underline{m}' and \underline{n}' have the same definition as \underline{m} and \underline{n} although independent thereof. The preparation of alkenylsuccinic anhydrides (I) from maleic anhydride and a C_{13} and/or C_{14} monoolefin mixture can be described, for a particular value of \underline{n} and \underline{m} , by the following scheme:



This reaction is generally conducted using an olefin/maleic anhydride ratio of between 3/1 and 1/1 and preferably 1.5/1. The temperature of this reaction can vary from 140 to 270°C but is preferably between 170 and 250°C, the yield being highest within this temperature range.

When the unreacted starting substances have been removed the mixture of alkenylsuccinic anhydrides (I) obtained can be brought directly into contact with the triethylenetetramine (II) under the conditions specified.

The condensation reaction is generally complete within a time period of between 1 and 6 hours, according to the chosen temperature. The water eliminated during the condensation reaction is removed from the reaction medium in order to displace the reaction equilibrium towards the products.

The product obtained in this manner does not need particular treatment and can in fact be used as such as an additive in liquid fuels and lubricants.

According to the present invention this product is added to liquid fuels and lubricants in a quantity sufficient to provide the desired dispersant and detergent activity and to inhibit rust formation on the metal parts in contact with the additive-containing fuels and lubricating oils.

The effective quantity is generally between 0.001 and 5% by weight and preferably between 0.01 and 3% by weight.

The additive can be directly added as such to the fuel or lubricant, or the addition can be facilitated by using a concentrate containing from 25 to 95% by weight and preferably from 50 to 70% by weight of additive dissolved in a solvent-diluent which in a preferred aspect of the present invention can be the actual fuel or lubricating oil to which the additive is to be added, eg. petrol, diesel oil, kerosene, mineral oils etc. Both the concentrate and the fuel or lubricant containing the additive of the present invention can contain other supplementary additives such as demulsifying agents, antifoaming agents etc. in the case of fuels, and anti-wear agents, viscosity improvers etc. in the case of lubricants. Both the concentrate and the final fuel or lubricant can also contain other detergent, dispersant and/or anti-rust agents in quantities insufficient to provide the required effect.

The following examples describe in greater detail the additive of the present invention and its preparation method, together with some of the tests used for evaluating the dispersant, detergent and anti-rust power of said additive.

EXAMPLE 1

Preparation of the new additive

An n-olefin mixture consisting of 58% tridecene and 40% tetradecene and having an average molecular weight of 187 (1069,79 g), maleic anhydride (373,76 g, 3,81 moles) and a small quantity of phenothiazine (1,5 g) acting as polymerization inhibitor during the synthesis are fed into a flask fitted with a mechanical stirrer, thermometer and reflux condenser.

The mixture is heated while stirring under a nitrogen atmosphere to 180°C, condensing the maleic anhydride and olefin vapours. As the reaction proceeds the temperature is gradually raised to 220°C and kept at this value for 13 hours. The excess olefin (413,65 g) and unreacted maleic anhydride (29,91 g) are recovered by distillation at 220°C, while progressively reducing the pressure in the reaction flask from atmospheric to (1330 Pa) (10 mmHg). The product obtained in this manner (1000 g, yield 92%) has a neutralization number of 200 mg KOH/g (titration by the ASTM D664 method), corresponding to an average molecular weight of 280,5. A part of the obtained product (500 g; 1,78 moles) and a silicone antifoaming agent (10 mg) are fed into a flask fitted with a mechanical stirrer, thermometer and condenser. The mixture is heated to 130°C under stirring, then using a dropping funnel triethylenetetramine of 91.4% purity (138,6 g; 0,87 moles) is gradually added over a period of one hour. During the addition the temperature rises spontaneously to 180°C.

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On termination of the addition the reaction mixture is kept at 160°C for two hours, removing the water which forms during the reaction by distillation. Water removal is completed by progressively reducing the pressure in the reaction flask from atmospheric to (1330 Pa) (10 mmHg) and maintaining the temperature at 150°C for 30 minutes.

The product obtained has a viscosity at 100°C of $4,96 \cdot 10^{-6} \text{ m}^2/\text{s}$ (4,96 cSt), a freezing point of -9°C, a nitrogen content of 8% and a base titre, determined by the ASTM D2896 method, of 157 mg KOH/g.

EXAMPLE 2

Evaluation of anti-rust power

a) In fuels

A steel pin is rotated for 24 hours in a vessel containing a mixture of 300 g of fuel (diesel oil or petrol) and 30 g of distilled water maintained at 60°C (ASTM D665/A test). The rust formed on the pin is then evaluated.

In the case of non-additived fuel the pin is completely covered with rust after 24 hours.

In contrast, if 50 ppm of the compound of Example 1 are added to the fuel, the pin is covered with only a few points of rust, whereas if 100 ppm of the additive of Example 1 are added the pin is completely free of rust.

b) In automotive lubricants

In the case of automotive lubrication oils the anti-rust power was evaluated both by the aforesaid ASTM D665/A test and by a Sequence IID engine test using a V-8 Oldsmobile engine bench-operated for 32 hours in accordance with the ASTM STP 315 procedure using as lubricant a control lubricant not containing the additive of Example 1 and, in a parallel test, the same lubricant but containing 0,15% of the product of Example 1. The control lubricant formulation was based on mineral oil containing 1,3% of zinc dithiophosphate, 4,5% of an ashless dispersant and 1,5% of a detergent consisting of a superbasic calcium sulphonate (12% of calcium by weight) having a viscosity at 100°C of $12,5 \cdot 10^{-6} \text{ m}^2/\text{s}$ (12,5 cSt). The result of the engine test is considered positive if the evaluation of the engine components at the end of the test, expressed as a score out of ten, exceeds 8,5.

In the ASTM D665/A test the control lubricant not containing the anti-rust additive gave a pin 50% covered with rust, whereas in the sequence IID engine test it gave an average rust score of 7,5. In contrast the lubricant containing 0,15% of the additive of Example 1 gave a pin completely free of rust in the ASTM D665/A test and an average score of 8,7 in the engine test.

EXAMPLE 3

Evaluation of detergent power

a) In diesel oil

The detergent power was evaluated by an engine injector detergency test using a commercial diesel oil without detergents as the control and the same diesel oil with 100 ppm of the product of Example 1 added. Specifically, a boosted Peugeot XD2S diesel engine fitted with DN OSD 252 Bosch injectors was used, bench-operated for 20 hours.

Before and after the test the injector throughput is measured at different needle lifts (0,1 and 0,3 mm), these measurements being used to calculate the percentage throughput reduction due to deposit formation.

In the case of the commercial diesel oil without additive, the average throughput reduction is 76,5%. With the diesel oil comprising 100 ppm of the product of Example 1, this average reduction is 60,5%, corresponding therefore to a reduction of 21% in the injector deposits compared with the diesel oil without additive.

b) In petrol

The detergent power was evaluated by an engine detergency test on the carburettor using a commercial petrol as control and the same petrol with 100 ppm of the product of Example 1 added. Specifically, a Renault R5 petrol engine was used, bench-operated in accordance with the CEC F-03-T-81. The evaluation is carried out using a conventional merit scale from 1 to 10, where 10 corresponds to the carburettor completely clean.

The petrol without additive merited a score of 3,7 in this engine test, whereas the petrol with 100 ppm of the product of Example 1 added merited a score of 8,8.

EXAMPLE 4

Evaluation of dispersant power

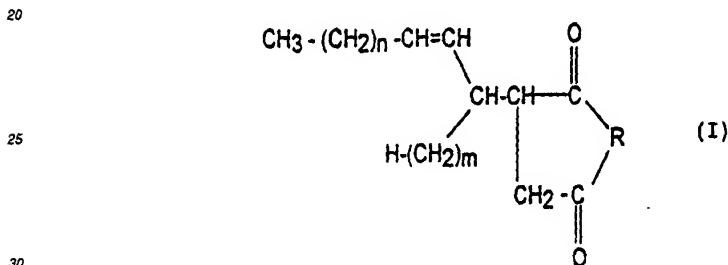
5 Diesel oil normally contains variable quantities of carbon particles in suspension. In diesel engines, where a filter system is incorporated into the fuel feed circuit, the accumulation of these deposits causes a progressive fall in fuel throughput until the filter is completely clogged.

The solubilizing/dispersing effect exercised on these deposits by the product of Example 1 was evaluated using a filter system simulating that used in diesel engines and measuring the time required to filter, under equal conditions, equal volumes of commercial diesel oil containing 100 ppm of the product of Example 1 and of the same diesel oil without additive.

In the first case the filtration time was 12 min and in the second case 26 min.

15 Claims

1. Use of the condensation product of a blend of alkenylsuccinic acids or acid anhydrides thereof, having the formula (I):



wherein

\underline{m} and \underline{n} are, independently of one another, 0 or an integer selected among the integers from 1 inclusive to 10 inclusive, the sum $(\underline{m} + \underline{n})$ being 9 or 10, and R is a bivalent group selected from -O- and (-OH; -OH), with triethylenetetraamine having the formula (II):

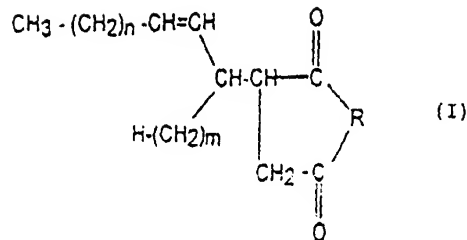


40 wherein the predominant product is a mixture of bis-succinimides and the condensation reaction takes place by directly heating, at a temperature of from 150°C to 200°C, a blend of (I) and (II), the molar ratio of (I) to (II) being 2,0, as an additive for improving, in an automotive liquid fuel or lubricating oil, the detergent, dispersing and rust-preventing properties.

2. Use according to Claim 1, characterized in that the additive is added in an amount in the range of 50 to 1500 ppm.

Patentansprüche

1. Verwendung des Kondensationsprodukts eines Gemisches aus Alkenylbernsteinsäuren oder deren Säureanhydriden gemäß der Formel (I)



worin m und n unabhängig voneinander 0 oder eine ganze Zahl, ausgewählt aus den ganzen Zahlen von einschließlich 1 bis einschließlich 10, bedeuten, die Summe $(m + n)$ 9 oder 10 bedeutet, und R aus $-\text{O}-$ und $-\text{OH}$ ausgewählt ist.
mit Triäthylentetraamin der Formel (II)

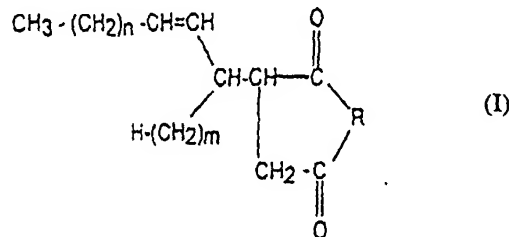


wobei das Hauptprodukt ein Gemisch aus Bissuccinimiden ist und die Kondensationsreaktion direkt durch Erwärmen bei einer Temperatur von 150°C bis 200°C eines Gemisches aus (I) und (II) stattfindet, das Molverhältnis von (I) zu (II) 2,0 beträgt,
als Additiv für die Verbesserung der Detergenz-, Dispersions- und Rostvorbeugungs-Eigenschaften in einem flüssigen Kraftfahrzeugbrennstoff oder -schmieröl.

- Verwendung nach Anspruch 1, dadurch gekennzeichnet, daß das Additiv in einer Menge im Bereich von 50 bis 1500 ppm zugegeben wird.

Revendications

- Emploi du produit de condensation d'un mélange d'acides alcényl-succiniques ou d'anhydrides de tels acides, de formule (I):



dans laquelle m et n représentent, indépendamment l'un de l'autre, 0 ou un nombre entier choisi parmi les nombres entiers de 1 à 10, bornes comprises, la somme $(m + n)$ valant 9 ou 10, et R représente soit $-\text{O}-$, soit deux groupes $-\text{OH}$,
avec de la triéthylènetétramine de formule (II):



le produit majoritaire étant un mélange de bis-succinimides, et la réaction de condensation étant effectuée par chauffage direct, à une température de 150 à 200°C , d'un mélange des composés (I) et (II) dans lequel le rapport

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molaire de (I) à (II) vaut 2,0,
comme adjuvant destiné à améliorer les propriétés détergentes, dispersantes et antirouille au sein d'un combustible liquide pour automobiles ou d'une huile lubrifiante.

- 5 2. Emploi conforme à la revendication 1, caractérisé en ce qu'on ajoute l'adjuvant en une proportion située dans l'intervalle allant de 50 à 1500 ppm.

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